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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US98/25721 <b>(22) International Filing Date:</b> 11 December 1998 (11.12.98)  <b>(71) Applicant (for all designated States except US):</b> HENKEL CORPORATION [US/US]; Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GOODREAU, Bruce, H. [US/US]; 11455 35 Mile Road, Romeo, MI 48065 (US). PRESCOTT, Thomas, J. [US/US]; 1601 Brentwood, Troy, MI 48098 (US). MILLER, Robert, W. [US/US]; 1510 West Predmore Road, Oakland, MI 48363 (US). ENGEL, Christopher, A. [US/US]; 34133 Cortland, Farmington, MI 48037 (US).  <b>(74) Agent:</b> WISDOM, Norvell, Jr.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).			<b>(81) Designated States:</b> AU, BR, CA, MX, TR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> COMPOSITION AND PROCESS FOR TREATING METAL SURFACES			
<b>(57) Abstract</b>  A metal substrate is provided with a coating that (i) provides substantial corrosion resistance, (ii) makes it possible to shape the substrate by roll forming and similar light cold forming operations without the need for any oil or wax lubricant, and (iii) has good adhesion to subsequently applied paint. This is achieved by coating the metal substrate surface with an aqueous liquid composition that contains acrylate polymer resin, wax, and hexavalent chromium and then drying this coating into place on the surface to produce the desired dry coating.			

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Description**COMPOSITION AND PROCESS FOR TREATING METAL SURFACES****FIELD AND BACKGROUND OF THE INVENTION**

This invention relates to treatment of a metal surface with an aqueous liquid composition that, before and/or during drying of the liquid composition into place on the surface, spontaneously reacts with the metal surface, without any application of electro-  
5 motive force from an external source, to produce on the metal a surface with better corrosion resistance than the original untreated metal surface. More particularly, this invention is related to a process that provides a corrosion protective treatment that also provides lubricating qualities, so that mechanical deformation of the surface can be more readily accomplished, without unacceptable damage to the surface, than can the same  
10 mechanical deformation of the original untreated metal surface. Still more particularly, the metal surface treated is an alloy of zinc and aluminum, and/or the lubricating quality of the surface is sufficiently good that a metal sheet or coil having at least one surface modified by the treatment can be roll formed and/or press molded without unacceptable surface damage and without the use of any additional lubricant material on the part of  
15 the treated metal surface that is being mechanically deformed.

Aluminum-zinc alloy coated steel sheets are steel sheets which have been coated with an alloy which consists of 4 - 75 % by weight of aluminum, the remainder being mainly zinc with traces of other components such as silicon, magnesium, cerium, lanthanum, or the like. At the present time at least two such types of sheet steel are being  
20 manufactured: low aluminum-zinc alloy coated steel sheets, which are coated with an alloy consisting of 4 - 10 % by weight of aluminum, the remainder consisting mainly of zinc with traces of magnesium, cerium, and/or lanthanum, and high aluminum-zinc alloy coated steel sheets, which are coated with an alloy consisting of 55 % by weight of aluminum, 43.4 % by weight of zinc, and 1.6 % by weight of silicon. If the thickness of  
25 the coated layer on these sheets is the same as that on otherwise similar hot-dip galvanized steel sheets, the corrosion resistance is improved by a factor of some 1.5 - 2 times in the case of the low aluminum-zinc coated steel sheets and by a factor of some 3 - 6 times in the case of the high aluminum-zinc alloy coated steel sheets. Furthermore the high aluminum-zinc alloy coated steel sheets also have heat reflecting properties and  
30 excellent resistance to heat. As a result of their excellent properties, these aluminum-zinc alloy coated steel sheets have found wide application as building materials in the form of roofing and walling materials, in civil engineering applications, .g., as guard

rails, sound insulating barriers, anti-snow fencing, or drainage gullies, as materials for automobiles, domestic appliances, and industrial machinery and, after having been painted, as replacements for painted steel sheets.

However, the coated layer on these aluminum-zinc alloy coated steel sheets provides less effective lubrication than does the substantially pure zinc such as is found on the surface of hot-dip galvanized steel when roll forming or press molding these materials. The surface of aluminum-zinc alloy is more susceptible to damage; the coated layer may become fused onto the forming rolls or the pressing dies as a result of the heat which is generated by friction during such operations; and metal powder which has become detached from the aluminum-zinc alloy coated sheet steel may become attached to the forming rolls or the pressing dies. This powder may accumulate in the corner parts of a molded product, or it may cause defects that blemish the external appearance of the product.

In the past these problems have been overcome by coating the surface of the aluminum-zinc alloy coated sheet steel with a lubricant such as oil or wax when carrying out shaping operations, in order to provide adequate lubrication at the surface of the aluminum-zinc alloy coated steel sheet. However, when such lubricating oils or waxes are used, there are disadvantages in subsequent processing and/or use. For example: the surface may be so slippery that an initially cylindrical coil of the finished material can readily be distorted by the force of gravity into a cone shape unless it is maintained strictly horizontal at all times when not mechanically restrained from such shape deformation; anything placed on an inclined surface of the coated lubricated material can more readily slip off than if the oil or wax were not present; and, if a coating is to be applied to the aluminum-zinc coated steel sheet after the shaping process, it is usually essential that all of the lubricating oil should be cleaned from the surface before applying any subsequent coating. Removing a lubricating oil or wax from the surface to a sufficient degree to assure uniformly good adhesion of the coating applied over it often is very difficult. Furthermore, when aluminum-zinc alloy coated steel sheet is shaped using a lubricating oil in the way described above, the lubricating oil becomes attached to the forming rolls or the pressing dies and if, at a later time, surface coated steel sheet is shaped using these same forming rolls or pressing dies, the lubricating oil often is transferred to the coated surfaces of these coated steel sheets, which are thereby stained. Any metal powder which is produced during the shaping process can become attached to the coated surface by way of the lubricating oil, so that it is necessary to clean the forming rolls or pressing dies thoroughly before carrying out such operations

in order to prevent the occurrence of this type of contamination; such cleaning is very troublesome.

Additionally, the surfaces of aluminum-zinc alloy coated steel sheets are often subjected to a chromate treatment in order to prevent the formation of rust while the material is being stored. However if the aluminum-zinc alloy coated steel sheets have been treated with a water soluble lubricating oil, chromating treatment can lead to problems with pollution due to the dissolution of the chromate later.

U. S. Patent 4,637,840 is believed to be the closest prior art. This teaches that a treatment composition consisting of water, hexavalent chromium, and a water soluble or water dispersible resin provides an external surface that does not need lubricating oil or wax. However, it has recently been found that the treatments provided according to the teachings of that patent are not always adequate to avoid a need for the use of lubricating oil to avoid surface damage during press and roll forming under current operating conditions. Accordingly, a major object of this invention is to provide a surface layer on metal substrates, particularly those of aluminum-zinc alloy, that will more reliably permit press and/or roll forming without the need for any additional lubrication with materials that (i) diminish the adhesion or blemish the surface appearance of a subsequently applied coating and/or (ii) make the surface so slippery as to cause substantial practical difficulties in further processing or use of the metal with a surface treatment formed according to this invention. Other alternative and/or concurrent objects will be apparent from the description below.

Except in the claims and the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred, however. Also, throughout the description, unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight or mass; the term "polymer" includes "oligomer", "copolymer", "terpolymer" and the like; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description or of generation *in situ* within the composition by chemical reaction(s) noted in the specification between one or more newly added constituents and one or more constituents already present in the composition when the other constituents are

added, and does not necessarily preclude unspecified chemical interactions among the constituents of a mixture once mixed; specification of constituents in ionic form additionally implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole and for any substance added to the composition; any counterions thus implicitly specified preferably are selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to an object of the invention; the word "mole" means "gram mole", and the word itself and all of its grammatical variations may be used for any chemical species defined by all of the types and numbers of atoms present in it, irrespective of whether the species is ionic, neutral, unstable, hypothetical, or in fact a stable neutral substance with well defined molecules; and the terms "solution", "soluble", "homogeneous", and the like are to be understood as including not only true equilibrium solutions or homogeneity but also dispersions that show no visually detectable tendency toward phase separation over a period of observation of at least 100, or preferably at least 1000, hours during which the material is mechanically undisturbed and the temperature of the material is maintained within the range of 18 - 25 °C.

#### BRIEF SUMMARY OF THE INVENTION

It has been found that at least the major object of the invention as stated above can be achieved by treatment with an aqueous liquid composition that comprises, preferably consists essentially of, or more preferably consists of, water and the following components:

- (A) dissolved, dispersed, or both dissolved and dispersed organic film-forming resin;
- (B) dissolved, dispersed, or both dissolved and dispersed wax that is not part of immediately previously recited component (A); and
- (C) dissolved, dispersed, or both dissolved and dispersed hexavalent chromium; and, optionally, one or more of the following components:
  - (D) dissolved, dispersed, or both dissolved and dispersed pH adjusting agent that is not part of any one of immediately previously recited components (A) through (C);
  - (E) dissolved, dispersed, or both dissolved and dispersed surfactant that is not part of any of immediately previously recited components (A) through (D);
  - (F) dissolved, dispersed, or both dissolved and dispersed trivalent chromium;
  - (G) dissolved, dispersed, or both dissolved and dispersed material selected from the group consisting of (i) reducing agents that are capable, at a specified tempera-

ture, of reducing hexavalent chromium in the composition to trivalent chromium and (ii) oxidation products from a reducing agent that has reduced some initially hexavalent chromium in the composition to trivalent chromium, said dissolved, dispersed, or both dissolved and dispersed material not being part of any of immediately previously recited components (A) through (F);

(H) dissolved organic solvent that is not part of any of immediately previously recited components (A) through (G);

(J) dispersed filler solid powder that is not part of any of immediately previously recited components (A) through (H); and

(K) colorant that is not part of any of immediately previously recited components (A) through (J).

For the purposes of this description:

- a "dissolved, dispersed, or both dissolved and dispersed film-forming resin" means a material that satisfies the following condition: when (i) the resin is dissolved, dispersed, or both dissolved and dispersed in an aqueous medium to form a liquid solution/dispersion that contains at least 20 % of the film-forming resin, (ii) said solution/dispersion is formed into a liquid film at least 2 millimeters in thickness, and (iii) said liquid film is dried at at least one temperature that is at least 40 °C, the resin forms a cohesive continuous solid body at the temperature of drying after drying is complete; and
- "wax" is defined as a substance that: (i) is a plastic solid at 25 °C under normal atmospheric pressure and (ii) melts in contact with the natural ambient atmosphere without visually evident decomposition at a temperature that is at least 55 °C.

#### DETAILED DESCRIPTION OF THE INVENTION AND ITS PREFERRED EMBODIMENTS

Component (A) preferably is selected from resins that, after drying from any solution/dispersion in which they may initially be present, are not soluble in water at 25 °C to an extent greater than, with increasing preference in the order given, 1.0, 0.5, 0.20, 0.10, 0.050, 0.020, 0.010, 0.0050, 0.0020, 0.0010, 0.00050, 0.00020, or 0.00010 % of the resin in water.

Independently, component (A) preferably is selected from polymers of vinyl monomers selected from the group consisting of hydrocarbons, halohydrocarbons, acrylic acid, methacrylic acid, maleic acid, and all esters, amides, and nitriles of organic acids. (Whether before or after polymerization, salts of any of these acids are to be understood as equivalent to the acids themselves.) If these polymers, as is usually preferred, have



as low a solubility in water before drying as they are preferred to have after drying, the resins will be predominantly dispersed rather than dissolved in the treatment composition. In such dispersions, a surfactant is normally required as a dispersing agent. The surfactants commonly used for this purpose in some (but not all) commercially supplied latexes, the preferred source for component (A), have not been observed to have any harmful effect on the properties of the compositions prepared with latexes containing them and if present are part of optional component (E) as described above, unless they are copolymerized into the polymer resin itself, in which instance they are part of component (A).

More preferably, component (A) is selected from polymers of monomers selected from the group consisting of acrylic acid, methacrylic acid, maleic acid, the esters of all of these acids, acrylonitrile, methacrylonitrile, acrylamide, and methacrylamide and still more preferably, in such polymers, the total number of millimoles of carboxylic acid and carboxylate salt moieties per gram of the dried resin is at least, with increasing preference in the order given, 0.030, 0.040, 0.050, 0.070, 0.080, 0.090, 0.100, 0.110, 0.120, 0.130, 0.135, or 0.140 and independently preferably is not more than, with increasing preference in the order given, 1.5, 1.0, 0.50, 0.40, 0.35, 0.30, 0.27, 0.24, 0.22, 0.200, 0.190, 0.180, 0.170, or 0.160.

Chemically, a wax to be used as component (B) in a composition or process according to this invention preferably is predominantly an organic substance selected from the group consisting of hydrocarbons, halohydrocarbons, halocarbons, alcohols, ethers, carboxylic acids, esters of carboxylic acids, ketones, and aldehydes. More preferably, the wax is polyethylene. Most if not all of the preferred waxes have scant solubility in water, and therefore are preferably added as dispersions to a mixture that constitutes, or after further additions will constitute, a composition according to the invention. Commercially available dispersions with fine dispersed particle size are preferably used. More particularly, the average particle size of a dispersion of wax that is part of component (B) in a composition according to the invention preferably is not more than, with increasing preference in the order given, 50, 40, 30, 20, 10, 5, 2, 1.0, 0.5, 0.20, 0.15, 0.12, 0.10, 0.08, or 0.06 micrometres. As with the acrylate polymers used in the same compositions, there is usually a dispersing agent required for a stable dispersion of this type; the dispersing agents in some but not all commercially supplied dispersions do not have any detrimental effect on a composition or process according to the invention; and when a dispersing agent for the wax component in a composition used according to the invention is present, this dispersing agent usually forms part of optional component (E).

Independently of its chemical nature, the melting point of a wax used in this invention preferably is at least, with increasing preference in the order given, 57, 65, 75, 85, 95, 105, 110, 115, 120, 125, or 129 °C and independently preferably is not more than, with increasing preference in the order given, 200, 180, 170, 160, 155, 150, 145, 140, 135, or 131 °C.

A substantial amount of wax component (B) is required to obtain the maximum resistance to damage in forming the finished product, but too large a fraction of wax can be disadvantageous. For example, too much wax may: reduce the corrosion resistance, if the wax by itself does not form a continuous protective coating as the acrylic component (A) does; make a substrate surface so slippery that it is very difficult to keep it coiled and/or to keep anything placed on an inclined surface of the coated substrate from sliding off; and/or cause undesired adhesion of the coated surface to another surface with which it is in contact, especially if the wax is low in melting point and the coated surface is exposed to heat while or shortly before it is in contact with another surface from which it is desired later to separate it. Specifically, the ratio by mass, on a dried basis, of wax component (B) to acrylate component (A) preferably is at least, with increasing preference in the order given, 0.020:1.00, 0.040:1.00, 0.050:1.00, 0.060:1.00, 0.065:1.00, 0.070:1.00, 0.075:1.00, 0.080:1.00, 0.085:1.00, 0.090:1.00, 0.095:1.00, 0.100:1.00, or 0.103:1.00 and independently preferably is not more than, with increasing preference in the order given, 0.50:1.00, 0.40:1.00, 0.30:1.00, 0.25:1.00, 0.20:1.00, 0.15:1.00, 0.13:1.00, or 0.11:1.00.

Any water soluble source of hexavalent chromium atoms may be used to provide necessary component (C) according to the invention. Examples include chromic acid (i.e.,  $\text{CrO}_3$ ), ammonium bichromate, potassium bichromate, sodium bichromate, ammonium chromate, potassium chromate, sodium chromate, and the like. The use of ammonium salts and/or chromic acid is preferred, in order to avoid the presence in a composition according to the invention of any non-volatile alkali component. Inasmuch as the pH value preferred for a working composition according to the invention is at least slightly alkaline, ammonium salts are preferred for at least part of component (C), but they are, at least for economy, preferably formed *in situ* by adding aqueous ammonia to an aqueous solution of chromic acid. Accordingly, the concentration of chromium in a composition according to the invention is usually measured as its stoichiometric equivalent as  $\text{CrO}_3$ , and this stoichiometric equivalent preferably has a ratio to the concentration of component (A) (on a dry basis) in the same composition that is at least, with increasing preference in the order given, 0.0010:1.00, 0.0020:1.00, 0.0050:1.00, 0.0075:1.00,

0.0100:1.00, 0.0110:1.00, 0.0120:1.00, 0.0130:1.00, 0.0135:1.00, 0.0140:1.00, 0.0145:1.00, 0.0150:1.00, 0.0155:1.00, 0.0158:1.00, or 0.0162:1.00 and independently preferably is not more than, with increasing preference in the order given, 0.50:1.00, 0.20:1.00, 0.10:1.00, 0.050:1.00, 0.040:1.00, 0.030:1.00, 0.025:1.00, 0.021:1.00, or 0.017:1.00. If the hexavalent chromium-containing material is too low in ratio to acrylate, the treated material usually has inadequate corrosion resistance and is often subject to blackening; while if the ratio of hexavalent chromium to acrylate is too large, the treatment composition may become unstable, will definitely generate higher pollution and/or pollution abatement costs if used in the large majority of jurisdictions where chromium is considered polluting, and will decrease the likelihood of achieving a transparent coating as is usually desired.

A working treatment composition according to the invention preferably has a pH value that is at least, with increasing preference in the order given, 3.0, 4.0, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, or 8.5 and independently preferably is not more than, with increasing preference in the order given, 11, 10.5, 10.0, 9.6, 9.2, 9.0, or 8.8. If the pH is too high or too low, the composition is likely to be unstable, because of precipitation and/or coagulation of at least part of its constituents. If most or all of the chromium present has been added as  $\text{CrO}_3$  and there is no other alkaline constituent in the composition, an alkalizing agent will usually be required as optional component (D) in order to achieve a highly preferred pH value. Any alkaline material may be used, but volatile ones such as ammonia and amines, for example, monoethylamine, diethylamine, triethylamine, and the like, and alkanolamines such as monoethanolamine, diethanolamine, and triethanolamine are preferred. At least for economy, simple ammonia, usually added as a concentrated solution in water, is most preferred.

As already noted above, generally optional component (E) is needed only to the extent necessary to disperse any insufficiently water-soluble constituents of components (A) and (B). If the substrate to be treated is exceptionally difficult to wet uniformly, additional surfactant may be needed for this purpose and if needed may generally be readily supplied from the knowledge of the art about wetting the particular surface concerned. A surfactant may also be needed in some instances for abatement of foaming, and again many suitable surfactants for this purpose are known to those skilled in the art. Otherwise, any additional surfactant is preferably omitted for economy.

Also as generally known in the art, the resistance to leaching of a chromium containing protective coating can be increased by converting part of the initially added hexavalent chromium to trivalent chromium (or, of course, by otherwise supplying trivalent

chromium to the composition and correspondingly reducing the content of hexavalent chromium). In general, no trivalent chromium is needed for this purpose in a working composition according to the invention, and if not needed is preferably omitted. In some instances, however, even when no trivalent chromium is desired in the working liquid composition as applied, it is advantageous for some chromium to be converted to a trivalent form during drying of the working composition into place on the substrate surface to be treated. This result may be achieved by using a working composition that contains an organic material that is not readily effective as a reducing agent for hexavalent chromium under the conditions of concentrations and storage and/or use temperature for the working composition, but that is effective as such a reducing agent at higher temperatures, higher concentrations, or both, which are achieved during drying of the liquid coating of working composition. For this purpose, it is preferable to utilize a reducing agent that does not cause any deterioration in the protective quality of the coatings formed. (It is widely believed, although not known with certainty, that the major reaction product from most of these reducing agents is carbon dioxide that escapes as a gas from the liquid composition before the liquid composition dries.) Various alcohols, glycols, sugars, starch, and like organic materials are suitable for this purpose, as known to those skilled in the art. For reasons considered in more detail below in connection with description of preferred drying conditions, propylene glycol has been found to be the most preferred of these latent reducing additives to a composition according to the invention to be used under normal commercial operating conditions. When propylene glycol is present in a composition according to the invention, the mass of propylene glycol present in the composition preferably has a ratio to total mass of chromium present in the same composition that is at least, with increasing preference in the order given, 0.30:1.00, 0.50:1.00, 0.70:1.00, 0.90:1.00, 1.10:1.00, 1.30:1.00, 1.50:1.00, 1.70:1.00, 1.90:1.00, 2.10:1.00, 2.30:1.00, 2.40:1.00, 2.50:1.00, 2.60:1.00, 2.70:1.00, 2.80:1.00, or 2.86:1.00 and independently preferably is not more than, with increasing preference in the order given, 10:1.0, 8.0:1.0, 6.0:1.0, 5.0:1.0, 4.5:1.0, 4.0:1.0, 3.5:1.0, or 3.0:1.0.

Optional component (H) of organic solvent is generally not needed and when not needed is preferably omitted. In some instances, however, desired constituents of components (A) and/or (B) may require the presence of organic solvent as an aid in practical preparation of a composition according to the invention. In any such instance, the amount is preferably kept to the minimum required. Alternatively, an organic solvent may be useful in removing contaminants from the substrate simultaneously with forming the desired protective coating according to the invention, but ordinarily better results will

be achieved if the substrate is conventionally cleaned before any contact with a composition according to this invention.

Optional component (J) of solid filler also is generally preferably omitted, because it tends to limit the ready extensibility of the coating formed and therefore to reduce the likelihood that this coating will remain in place during alterations of the shape of the metal substrate. However, use of a filler can substantially reduce the cost of the treatment and sometimes may be preferred for that reason. Numerous finely divided solids such as clays, colloidal silica and silicates, crushed limestone, and the like are known in the art and may be employed in such instances.

Optional colorant component (K) has no technical effect on the invention, but may be preferred in some instances for aesthetic reasons. Ordinarily, the dried coating formed will have sufficient color to be readily visible, but if exceptionally thin layers and/or exceptionally low fractions of chromium are used, a colorant may be preferred to furnish visual assurance of the presence of the coating. When a coloring is desired, numerous suitable dyes and pigments to achieve such a result are known to those skilled in the art.

A liquid surface treatment composition according to the invention may be coated onto the substrate by any effective method, such as dipping, spraying, brushing, roll coating, or using an air knife or an electrostatic coating technique, preferably after removing any grease or other soil from the surface of the substrate, to form a liquid coating over the substrate to be treated according to the invention. The coating may be formed on all surfaces of the substrate or on selected portions of the surface only, depending on the positioning of the liquid film from which the dry film is formed.

After the liquid coating has been formed and put into place on the part of the substrate intended to be covered, the non-volatile contents of the coating are dried into place on the substrate surface to be treated, preferably without any intermediate rinsing. As is generally known in the art, any particular polymer or mixture used for component (A) will ordinarily have a "minimum film forming temperature" that the coating must reach while some water still remains in it, in order to assure that a continuous film will be formed. The drying operation of a process according to this invention preferably achieves this minimum film forming temperature for component (A) of the liquid film actually being dried.

If the minimum film forming temperature is low enough, the drying may be accomplished simply by exposure to the ambient natural atmosphere at less than 100 % relative humidity. The most preferred materials for component (A), however, have a

minimum film forming temperature that is above normal ambient temperature in any space where the temperature is controlled for human comfort. For this reason and for increased process speed, ordinarily in commercial practice according to the invention drying preferably is accompanied by heating, for example in an oven, with a hot forced air drier, an infrared heater, or an induction heating device to convert the liquid film into an adherent dry coating over the surface of the substrate to be protected.

Particularly when high speed air flow is used, even air temperatures well above the minimum film forming temperature may not succeed in achieving continuous, crack-free coatings, presumably because too much water evaporates before the polymer content of liquid coating reaches its minimum film forming temperature. If such a phenomenon is observed, the temperature of heating should be raised until cracking or other discontinuities in the film do not occur. If there is substantially no air flow rate with respect to the liquid film, a peak metal temperature of 43 °C is sufficient to assure continuous coatings from the most preferred compositions according to the invention as described herein, but with strongly forced air, peak metal temperatures as high as 350 °C may be needed. Under specific process conditions, a suitable drying temperature that assures achieving at least the minimum film forming temperature for the acrylate polymer component in a liquid film composition according to the invention, along with otherwise satisfactory results, can be determined by minimal experimentation. A suitable drying temperature will depend on such factors as: whether heat is supplied by radiation, by transfer from a heat transfer fluid such as air, or by other methods or combinations of methods; the direction with respect to the liquid coating from which heat is primarily supplied; and the relative velocity between the liquid coating and the heat transfer fluids if any are used.

In addition to the effect of drying temperature on whether a crack free coating is formed from a particular composition according to the invention, it has been found that the peak substrate metal temperature reached during drying of a liquid coating to convert it into a solid coating according to this invention is a critical factor in the stabilization of the chromium content of the dried composition against leaching during later contact of the solid coating with water. To minimize leaching, a peak metal temperature of at least as much as 88 °C is preferred over any lower temperature, and under many conditions of drying with some compositions according to the invention even substantially higher temperatures than this are required to minimize leaching. However, a high peak metal temperature requires a large energy input in the drying process. This requires a substantial cost for energy to supply the large energy input required.

Furthermore, in some instances the necessary energy input to achieve such a high peak metal temperature may not be available from the equipment in place where a process according to the invention is desired. Still further, high peak metal temperatures may result in deterioration of other corrosion protective qualities of the coatings formed, even though chromium leaching is reduced. To achieve an optimum balance among these various factors, under practical conditions where a chromium leaching rate of up to 10 %, during either 24 hours of exposure to water at 18 - 22 °C or 30 seconds of exposure to water at 49 °C, is acceptable for articles that have been coated according to the invention and then allowed to age for at least 5 days between coating and leach testing, the peak metal temperature achieved during drying preferably is at least, with increasing preference in the order given, 43, 48, 53, 58, 63, 68, 73, 78, 83, 88, 93, 98, 103, 108, 113, 117, or 121 °C and independently preferably is not more than, with increasing preference in the order given, 205, 195, 185, 175, 165, 155, 145, 135, 130, or 125 °C. (Two suitable methods for determining peak metal temperatures are described as part of the examples below.)

Unless the metal substrate has a substantial chromium content, the amount of coating formed per unit area of the substrate coated may conveniently be determined by measuring only the chromium content of the coating formed by means of an X-ray emission spectrometer; the total solids content of the coating may then be calculated from the known ratio of the chromium content to the total mass of the coating. When the dried film contains about 1 % of chromium, measured as the element as is normally preferred, the mass of chromium per unit area of the substrate coated preferably is at least, with increasing preference in the order given, 1.0, 3.0, 5.0, 7.0, 8.0, 9.0, 9.5, 10.0, 10.5, 11.0, 11.4, or 11.7 milligrams per square meter (hereinafter usually abbreviated as "mg/m<sup>2</sup>") and independently preferably is not more than, with increasing preference in the order given, 100, 50, 40, 30, 25, 20, 17, 14, or 12 mg/m<sup>2</sup>. If the fraction of chromium in the coating differs widely from 1 %, these values should be adjusted correspondingly to result in approximately the same total film masses per unit area.

The coefficient of sliding friction of a sliding contactor of stainless steel against a surface treated according to the invention preferably is not more than, with increasing preference in the order given, 0.270, 0.265, 0.260, 0.255, 0.250, 0.245, 0.240, 0.235, or 0.230. If the coefficient of sliding friction is more than 0.270, fairly frequent cracking and/or flaking of the protective coating applied is likely to result during forming operations that result in corners with a radius of curvature of 1 millimeter or less, and such corners are not particularly unusual in the forming operations to which materials treated

according to this invention are subjected. The probability of any such undesirable cracking and/or flaking during forming operations in normal commercial practice has been found to decrease as the coefficient of sliding friction decreases from 0.270, and when it was 0.230, thousands of meters of substrate have been processed without a single observation of cracking or flaking of the protective coating during forming operations that form sharp corners.

Still lower coefficients of sliding friction than 0.230 do not cause any technical disadvantage during a forming operation, but may be disadvantageous later because coiled sheets with such a low coefficient of sliding friction can more readily slip spontaneously under the influence of natural gravity from their desired cylindrical shape into a partly conical shape that makes their mechanical handling more problematical. For this reason, independently, the coefficient of sliding friction produced in a process according to this invention preferably is at least, with increasing preference in the order given, 0.020, 0.050, 0.080, 0.10, 0.12, 0.14, 0.16, or 0.18.

The coefficient of sliding friction of a surface may conveniently be measured on a draw bench equipped to record continuously as a function of time the force required to draw a standard weighted contactor at a constant speed across the surface. Such measurements show that a high initial force is required to cause the weighted contactor to begin to move, while a slightly fluctuating but (usually) substantially lower force is sufficient to keep the contactor moving after it has begun to do so. The average value of this latter force, divided by the force measured in the same units of the contactor against the surface across which it is being drawn, yields as a quotient the coefficient of sliding friction.

In contrast to the coefficient of sliding friction, the coefficient of static friction of a coating according to this invention may advantageously be considerably higher in value than the coefficient of sliding friction, in order to reduce the incidence and severity of the possible difficulties already noted above that can occur with a very slippery surface for the final substrates treated according to this invention. The coefficient of static friction may conveniently be measured by resting a weighted contactor near one end of an initially horizontal but inclinable plane having a surface for which the coefficient of static friction is to be determined, and then gradually increasing the inclination of the plane until the weighted contactor begins to slip. The tangent of the angle to the horizontal that the inclined plane makes when the contactor just begins to slip is the coefficient of static friction. For measurements of static friction reported hereinbelow, neoprene rubber was used as the sliding contactor, and with this material, the coefficient of



static friction against a dry surface produced by a treatment according to this invention (before or without any additional coating that may be applied over the surface produced by a treatment according to the invention) preferably is at least, with increasing preference in the order given, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, or 1.00.

5 The invention and its benefits may be further appreciated by consideration of the following, non-limiting, examples and comparison examples.

The following candidate sources of components (A), (B), and (C) as described above were tested. (Short identifying letters and/or numbers as noted below have been arbitrarily assigned to these sources for use in later tables.)

10 FOR COMPONENT (A):

Latexes Commercially Supplied by Rohm & Haas:

H2 = Rhoplex™ HA-12: (45 % solids, pH ≈ 3.0 )

H6 = Rhoplex™ HA-16: ( 45.5 % Total Solids, pH ≈ 3.0 )

A7 = Rhoplex™ AC-73 or AC-73T (replacement for AC-73): (46.5 %  
15 Total Solids, pH ≈ 9.5 )

MC = Maincote™ HG-54: (41.5 % Total Solids, pH ≈ 7.5 )

MV = Rhoplex MV-23LO: (43 % Total Solids, pH ≈ 8.5 )

Latexes Commercially Supplied by ZENECA Resins:

N2 = Neocryl™ A625 (45 % Total Solids )

20 N4 = Neocryl™ A640

Other Latex:

AL = Arolon™ 870-W-51 (supplied by Reichhold)

Mixed Latexes:

AA = 50 % Rhoplex HA-12 + 50 % Rhoplex AC-73

25 AJ = 50 % Rhoplex HA-16 + 50 % Rhoplex AC-73T

AR = 20 % Rhoplex HA-16 + 80 % Rhoplex AC-73T

FOR COMPONENT (B):

AX = Unithox™ D-300 (commercially supplied by Petrolite Corp.; 23.5 % solids  
dispersion in water of molecules of ethoxylated straight chain primary  
30 alcohols averaging about 50 carbon atoms each in the alcohol portion  
and about 50 % of their mass in each of the alcohol portion and the  
ethoxylate portion)

AQ = Aquaslip™ 671 (commercially supplied by Langer & Co.; 40 % solids;  
polyethylene wax emulsion)

35 ME = Mich m™ Emulsion 39235 (commercially supplied by Michelman Inc.; 35

% solids; pH  $\approx$  10; polyethylene wax emulsion. This was tested only briefly, because compositions including it were observed to provide substantially less corrosion protection than those made with most of the other wax dispersions tried. Reduced corrosion protection is believed to be associated with the presence of a nonionic surfactant in this dispersion.)

AZ = Jonwax™ 26 (commercially supplied by Johnson Polymer Div. of S. C. Johnson & Sons, Inc.; 25 % solids; pH  $\approx$  9.5; polyethylene wax emulsion)

FOR COMPONENT (C):

S1 = 81.0 % deionized (hereinafter usually abbreviated as "DI") water + 10.0 % Chromic Acid + 9.0 % NH<sub>4</sub>OH (containing 29.7 % NH<sub>3</sub>)

S1A = 90 % water + 10 % chromic acid

S4 = Composition 1A partially reduced (with an organic material that leaves no substantial residue in the composition) so that its chromium content is 70 % Cr(VI) and 30 % Cr(III)

FOR COMBINED COMPONENTS (A) AND AT LEAST PART OF (C):

AS = 99.44 % Rhoplex AC-73T + 0.56 % of 20 % Chromic Acid Solution in H<sub>2</sub>O

AM = 50 % AS + 50 % MV

SPECIFIC EXAMPLE AND COMPARISON EXAMPLE GROUP 1, WITH CHROMIUM LEACHING TESTS

Compositions, drying conditions, coating weights, and leaching results are shown in Table 1 below for coatings on test panels of commercially supplied steel coated on both sides with an alloy of 55 % aluminum with the balance predominantly zinc. Unless otherwise specified, for all entries in Table 1: drying is in a convection oven with natural air as the heat transfer fluid; the dried samples are allowed to age for at least four days between drying and leach testing; the leaching test is for 15 seconds under rapidly running municipal water at 26 to 32 °C; the amount of chromium is measured before and after leaching by a Portaspec™ X-ray emission spectrometer; and the times of exposure during drying that are shown are only approximate, because the termination of exposure is determined by the time required to reach the peak metal temperature specified. The peak metal temperature was measured with the aid of temperature sensitive paper manufactured by the Paper Thermometer Co., Greenfield, New Hampshire. This temperature sensitive paper undergoes an irreversible blackening when its temperature exceeds a value specified on the paper itself or a package containing it. In most instances, one or more small squares of temperature sensitive paper with a particular indicator temperature were attached directly to a sample of the substrate material that had been coated

Table 1

ID Number	Coating Composition, Parts by Volume-Material for Component:			Drying Conditions			Chromium Coating, mg/m <sup>2</sup>	Percent of Chromium Leached
	(A)	(B)	(C)	Air °C	Seconds of Exposure Time	Peak Metal Temperature Reached, °C		
1	9-AJ	1-S1	none	343	3	68	9.0	> 50
2	9-AJ	1-S1	1-AZ	288	10	82	23	25
3	9-AJ	1-S1	1-AZ	316	20	143	8.9	20
4	9-AJ	1-S1	1-AZ	260	30	143	4.4	9.4
5	9-AJ	1-S1	1-AZ	343	20	168	17	1.2
6	9-AJ	1-S1	1-AZ	343	30	212	19	0.2
7	12-AJ	1-S1	1-AZ	399	3	99	13	10
8	12-AJ	1-S1	1-AZ	316	20	143	14	3.7
9	10-AJ	1-S1	1-AZ	Infrared heating		260	30	2.1*
10	15-AJ	1-S1	1-AZ	260	35	149	8.8	6.7*
11	9-AJ	1-S1	1-AZ	177	30	93	8.9	39*
12	21-AJ	1-S1	1-AZ	177	30	93	7.6	9.0*
13	30-AJ	1-S1	1-AZ	177	30	93	5.4	3.3*
14	15-A6	1-S1	2-AZ	204	25	121	11.5	32
15	15-AR	1-S1	1-AZ	204	25	121	8.8	< 1
16	15-HG	1-S1	2-AZ	204	25	121	10.2	1.0
17	15-AA	1-S1	1-AZ	204	25	121	12.2	7.0
18	15-A2	1-S1	2-AZ	204	25	121	12.2	26
19	15-AL	1-S1	2-AZ	204	25	121	8.4	17
20 <sup>11</sup>	15-AR	1-S1	1-AZ	204	25	121	3.3	3.7
21	15-N2	1-S1	1-AZ	204	25	121	10.8	82
22	15-AR	1-S1A	1-AZ	204	25	121	10.9	3.3
23	15-AR	1-S4	2-AZ	204	25	121	9.1	1.8
24 <sup>12</sup>	15-AR	1-S1	1-AZ	204	25	121	9.7	< 1
25	15-AR	1-S1	1-AZ	399	7	121	11.2	13
26	18-AS	1-S1	1-AX	204	25	121	12.5	< 1
27	18-AQ	1-S1	0.6-AQ	204	25	121	12.2	< 1
28	18-AS	1-S1	0.65-ME	204	25	121	11.4	11.4**
29 <sup>13</sup>	18-AS	1-S1	2-AZ	204	25	121	9.8	4.2**
30 <sup>14</sup>	18-AS	1-S1	0.5-ME	204	25	121	10.0	< 1**
31 <sup>15</sup>	18-AS	1-S1	0.5-ME	204	25	121	10.6	< 1**
32	19-MV	1.2-S1	0.5-AZ	204	25	121	11.2	< 1**

... This table is continued on the next page ...

ID Number	Coating Composition, Parts by Volume-Material for Component:			Drying Conditions			Chromium C ating, mg/m2	Percent of Chromium Leached
	(A)	(B)	(C)	Air °C	Seconds of Exposure Time	Peak Metal Temperature Reached, °C		
33 <sup>16</sup>	18-AS	1.0-S1	1.0-AZ	204	25	121	6.6	15**
34	18-AM	1.1-S1	1.0-AX	204	25	121	9.9	5.8**
35 <sup>16</sup>	18-AS	1.0-S1	1.0-AZ	204	25	121	9.8	< 1**
36	21-N4	1.0-S1	1.0-AX	204	25	121	8.5	13**
37 <sup>16</sup>	21-N4	1.0-S1	1.0-AX	204	25	121	11.3	5.8**

Footnotes for Table 1

\*The tests that produce these results are run less than three days after the substrates had been coated.

\*\*These tests are for leaching by immersion for 24 hours in water at 18 - 22 °C.

<sup>11</sup>This composition also contains sugar.

<sup>12</sup>This composition also contains methanol.

<sup>13</sup>This composition also contains 0.1 part of propylene glycol.

<sup>14</sup>This composition also contains 0.05 part of propylene glycol.

<sup>15</sup>This composition also contains 0.3 part of propylene glycol.

<sup>16</sup>This composition also contains 1.0 part of propylene glycol.

with a composition to be tested, and several such samples were exposed for different intervals in a particular oven at a particular temperature, until conditions for attaining at least the desired peak metal temperature were determined; at least one sample to be measured for leaching is then exposed to the conditions so determined, usually without any temperature sensitive paper on the substrate on which actual leaching is measured. Alternatively, one or more squares of temperature sensitive paper are placed directly on the same substrate on which the leaching value is later measured, on either a coated or an uncoated portion of the substrate sample, so that the blackening of the temperature sensitive paper can be observed either during its actual drying or afterward. The use of temperature sensitive paper accordingly measures directly only a minimum peak metal temperature, but by advance testing as described above, or by the use of temperature sensitive paper squares with different indicator temperatures on a single coated substrate, it is possible reasonably to assure that the actual peak metal temperature is not further above the minimum than the intervals between temperature sensitive papers with different indicator temperatures, about 6 °C.

#### SPECIFIC EXAMPLE AND COMPARISON EXAMPLE GROUP 2, WITH COATING CONTINUITY TESTS

In this group, only drying conditions were varied. The composition coated contained 58 % of Rhoplex™ AC-73T, 4.4 % of "S1" partially neutralized chromic acid

solution as defined above, and 11 % of "AZ" wax dispersion as defined above, with the balance being water. This liquid composition was coated onto test substrates as for Group 1, but the substrates were coated on only one side and placed immediately after coating on a laboratory hot plate set to a known temperature, with the wet coated side up and exposed to the natural atmosphere. The peak metal temperature in these experiments was determined with the use of temperature sensitive paper generally as described above, either by advance experiments with the hot plate or by squares of the temperature sensitive paper directly on the substrate tested. In some instances, no supplemental air flow other than that produced by convection was used, while in others a stream of forced air was directed along the surface as it dried. The dried coatings were examined visually to determine whether they were hazy or transparent and the coatings were further examined microscopically to determine the presence or absence of cracks. Results are shown in Table 2 below. These results indicated that the minimum film forming temperature of the polymer in the latex used is between 28 and 38 °C, consistent with the report of the manufacturer of the latex that the minimum film forming temperature is 35 °C. However, even with a contact heater far above that temperature, the coating can be made discontinuous by too high an air flow over its outer surface during drying.

Table 2

ID Number	Cr, mg/m <sup>2</sup>	Hot Plate, °C	Augmented Air?	Hazy or Clear?	Cracked?
1	33	28	No	Hazy	Yes
2	13	25	Yes	Hazy	Yes
3	19	38	No	Clear	Partly
4	19	38	No	Hazy	Yes
5	17	38	Yes	Hazy	Yes
6	18	43	No	Clear	No
7	16	71	No	Clear	No
8	23	71	Yes	Hazy	Yes

## CLAIMS

1. A process for treating a metal surface to reduce the coefficient of sliding friction thereon, said process comprising operations f:
- 5 (I) forming over said metal surface a coating of a liquid composition that before, during, or both before and during drying reacts with said metal surface to produce a modified solid surface with a lower coefficient of sliding friction than said metal surface; and
- (II) drying said coating of liquid composition into place on said metal surface over which it was formed in operation (I), without intermediate rinsing,
- 10 wherein the improvement comprises using a liquid composition that comprises water and the following components:
- (A) dissolved, dispersed, or both dissolved and dispersed organic film-forming resin;
- (B) dissolved, dispersed, or both dissolved and dispersed wax that is not part of immediately previously recited component (A); and
- 15 (C) dissolved, dispersed, or both dissolved and dispersed hexavalent chromium.
2. A process according to claim 1, wherein the mass of wax component (B) in said liquid composition has a ratio to the mass of resin component (A) in said liquid composition, both of these masses being on a dry basis, that is at least about 0.60:1.0.
3. A process according to claim 2, wherein the mass of the stoichiometric equivalent as  $\text{CrO}_3$  of the hexavalent chromium present in said liquid composition has a ratio to the mass, on a dry basis, of the resin component (A) in said liquid composition that is at least about 0.0050:1.0.
- 20 4. A process according to claim 3, wherein resin component (A) is selected from the group consisting of polymers of acrylic acid, methacrylic acid, maleic acid, the esters of all of these acids, acrylonitrile, methacrylonitrile, acrylamide, and methacrylamide.
- 25 5. A process according to claim 4, wherein wax component (B) is a polyethylene wax with a melting point in a range from about 85 to about 150 °C.
6. A process according to claim 5, wherein:
- the ratio of the mass of wax component (B) to the mass of resin component (A), both on a dry basis, is from about 0.090:1.00 to about 0.15:1.0;
- 30 - the ratio of the mass of the stoichiometric equivalent as  $\text{CrO}_3$  of the content of hexavalent chromium to the mass, on a dry basis, of resin component (A) is from about 0.0140:1.00 to about 0.030:1.00; and
- during operation (II), the metal substrate reaches a temperature of at least about

88 °C.

7. A process for treating a metal surface to reduce the coefficient of sliding friction thereon, said process comprising operations of:

(I) forming over said metal surface a coating of a liquid composition that before, during, or both before and during drying reacts with said metal surface to produce a modified solid surface with a lower coefficient of sliding friction than said metal surface; and

(II) drying said coating of liquid composition into place on said metal surface over which it was formed in operation (I), without intermediate rinsing,

wherein the improvement comprises using a liquid composition that has been made by mixing with a first mass of water at least the following additional masses:

(A) a second mass of organic film-forming resin that is spontaneously water soluble, dissolved in water, dispersed in water, or any two or more of spontaneously water soluble, dissolved in water, and dispersed in water;

(B) a third mass of wax that is not part of said second mass and that is spontaneously water soluble, dissolved in water, dispersed in water, or any two or more of spontaneously water soluble, dissolved in water, and dispersed in water; and

(C) a fourth mass of a source of hexavalent chromium that is spontaneously water soluble, dissolved in water, dispersed in water, or any two or more of spontaneously water soluble, dissolved in water, and dispersed in water.

8. A process according to claim 7, wherein said third mass has a ratio to said second mass that is at least about 0.60:1.0.

9. A process according to claim 8, wherein the mass of the stoichiometric equivalent as  $\text{CrO}_3$  of the hexavalent chromium in said fourth mass has a ratio to the mass, on a dry basis, of the resin component (A) in said liquid composition that is at least about 0.0050:1.0.

10. A process according to claim 9, wherein the resin in said second mass is selected from the group consisting of polymers of acrylic acid, methacrylic acid, maleic acid, the esters of all of these acids, acrylonitrile, methacrylonitrile, acrylamide, and methacrylamide.

11. A process according to claim 10, wherein the wax in said third mass is a polyethylene wax with a melting point in a range from about 85 to about 150 °C.

12. A process according to claim 11, wherein:

- the ratio of said third mass to said second mass is from about 0.090:1.00 to

about 0.15:1.0;

- the ratio of the mass of the stoichiometric equivalent as  $\text{CrO}_3$  of the content of hexavalent chromium in said fourth mass to said second mass is from about 0.0140:1.00 to about 0.030:1.00; and
- 5 - during operation (II), the metal substrate reaches a temperature of at least about 88 °C.

13. A process according to any one of claims 1 through 12, wherein the dried coating formed in operation (II) contains at least 5 mg/m<sup>2</sup> of chromium.

14. A process according to claim 13, wherein the dried coating formed in operation  
10 (II) has a coefficient of sliding friction against stainless steel that is not more than 0.250.

15. A process according to any one of claims 1 through 12, wherein the dried coating formed in operation (II) has a coefficient of sliding friction against stainless steel that is not more than 0.250.

16. A process according to claim 15, wherein the metal substrate surface coated is  
15 an alloy of aluminum and zinc.

17. A process according to any one of claims 1 - 12 and 14, wherein the metal substrate surface coated is an alloy of aluminum and zinc.

18. A process according to claim 13, wherein the metal substrate surface coated is an alloy of aluminum and zinc.

20 19. A liquid composition of matter useful as a treatment composition in a process according to claim 6, said liquid composition comprising water and the following components:

- (A) a mass of dissolved, dispersed, or both dissolved and dispersed organic film-forming resin;
- 25 (B) a mass of dissolved, dispersed, or both dissolved and dispersed wax that is not part of immediately previously recited component (A); and
- (C) a mass of dissolved, dispersed, or both dissolved and dispersed hexavalent chromium,

wherein:

- 30 - the ratio of the mass of wax component (B) to the mass of resin component (A), both on a dry basis, is from about 0.090:1.00 to about 0.15:1.0; and
- the ratio of the mass of the stoichiometric equivalent as  $\text{CrO}_3$  of the mass of hexavalent chromium to the mass, on a dry basis, of resin component (A) is from



about 0.0140:1.00 to about 0.030:1.00.

20. A liquid composition of matter useful as a treatment composition in a process according to claim 12, said liquid composition having been made by mixing with a first mass of water at least the following additional masses:

- 5 (A) a second mass of organic film-forming resin that is spontaneously water soluble, dissolved in water, dispersed in water, or any two or more of spontaneously water soluble, dissolved in water, and dispersed in water;
- (B) a third mass of wax that is not part of said second mass and that is spontaneously water soluble, dissolved in water, dispersed in water, or any two or more
- 10 of spontaneously water soluble, dissolved in water, and dispersed in water; and
- (C) a fourth mass of a source of hexavalent chromium that is spontaneously water soluble, dissolved in water, dispersed in water, or any two or more of spontaneously water soluble, dissolved in water, and dispersed in water,

wherein:

- 15 - the ratio of said third mass to said second mass is from about 0.090:1.00 to about 0.15:1.0;
- the ratio of the mass of the stoichiometric equivalent as  $\text{CrO}_3$  of the content of hexavalent chromium in said fourth mass to said second mass is from about 0.0140:1.00 to about 0.030:1.00.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/25721

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B05D 3/02, 1/18; C23C 22/07; C08J 3/38

US CL : 148/253; 427/388.4, 435; 524/407

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/253; 427/388.4, 435; 524/407

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
APS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,753,740 A (ODAWA et al.) 19 May 1998, columns 12-18 and the examples.	1-20
X	US 5,496,652 A (SASAKI et al.) 5 March 1996, columns 8-10.	1-20
A	US 4,637,840 A (FUJII et al.) 20 January 1987.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents.	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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